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Procedia Engineering 161 (2016) 73 – 78

Procedia Engineering

www.elsevier.com/locate/procedia

World Multidisciplinary Civil Engineering-Architecture-Urban Planning Symposium 2016, WMCAUS 2016

Effect of Binder Composition on the Structure of Cement Paste and on Physical Properties and Freeze-Thaw Resistance of Concrete

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Abstract

The primary objective of this study was to determine how differences in the composition of the binder made with Portland cement, slag and/or fly ash affect the modification of the cement paste structure and the properties of concrete with respect to its freeze/thaw resistance. The test results show that the use of mineral additions (fly ash or a mixture of fly ash and slag) does not guarantee the impermeability and the frost resistant structure of concrete. The concrete behaves as expected up to the slag level of 20 % by mass of the cement. The results from the tests conducted on non-air entrained concretes with W/B ratio of 0.45 (limiting value for concrete exposure class XF4) show that the concrete mix in any case should be air entrained when mineral additions are to be used.

Peer-review under responsibility of the organizing committee of WMCAUS 2016

Keywords: structure; porosity; paste; concrete; permeability; freeze-thaw resistance;

1. Introduction

Water-to-cement (W/C) ratio is the basic parameter that characterises porosity of a cement matrix. It has a decisive influence on porosity and hence on permeability of concrete. Modern technology of concrete offers considerable scope for cementitious material modifications through the use of chemical active additives. At a given age and W/B, concrete with portland cement generally has a higher total porosity than blended cement [6]. The addition of slag reduces capillary pore numbers, which decrease further with the hardening time. Cement pastes with the addition of fly ash are usually slightly more porous after a short hardening time than the Portland cement-based pastes [5]. The addition

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Peer-review under responsibility of the organizing committee of WMCAUS 2016
doi:10.1016/j.proeng.2016.08.500

of siliceous fly ash to GGBS cement is particularly suitable for liquid concrete mixtures used in foundations. Fly ash increases the portion of fines, improves mix pumpability, and reduces dynamics, shrinkage and heat of hydration. Concrete from slag cements with fly ash addition has high strength after 28 days and after longer time e.g. 180 days. Resistance of concrete from slag cements with fly ash addition on the action of lower temperature is still an engineering problem requiring further studies [3]. Giergiczny et al. [4] confirm that worse air-voids structure parameters were observed in the mixtures with the slag. Studies have found Bilek et al. [1, 2] that the use of three-component binders can eliminate the need for air entraining.

Determination of parameters describing the porosity structure of a cement material is a complex task due to a wide range of pores size in concrete and difficulties in preparing specimens for testing [9]. The impermeability of concrete is determined by its permeation, which describes three transport mechanisms in a porous material: diffusion, sorption and permeability. In the mature cement paste, permeability is dependent on the size, shape and concentration of gel particles as well as on whether capillaries maintain their continuity. Nyame and Illston [8] found a good relation between the maximum continuous pore radius, measured using mercury porosimeter, and permeability of hardened cement paste. Their studies indicate that the decrease of permeability with paste maturing time is caused by the reduction in capillary pore proportion and their continuity. At the same time, the reduction in the number of capillary pores progresses faster with decreasing W/C ratio [8]. Müller [7] studied resistance of concrete to chloride migration, which also depends on the type and amount of mineral additions used. The most resistant concretes are those made with the highest content of slag. The time needed for concrete to reach maturity under adequate humidity has a fundamental influence on its porosity, especially that of concretes with mineral additions.

This study is aimed at determining the effect of varied compositions of the binder made with Portland cement, slag and/or fly ash on the modification of cement paste structure and freeze-thaw resistance-related properties of concrete.

2. Materials and Methods

The primary aim of this research was to determine how variations in the composition of binders containing Portland cement, slag and/or fly ash affect the modification of the cement paste structure and properties of concrete with respect to freeze-thaw resistance. The testing programme comprised two stages. In stage one, the effect of the binder composition on the cement paste microstructure was studied using mercury porosimetry (MIP) and scanning electron microscopy (SEM). Tests on concretes were performed in the second stage of the programme and included the determination of their physical characteristics (absorption, n_w, permeability, Q), compressive strength, fc, and freeze-thaw resistance (slab test), m_{56}.

The binder constituents included Portland cement (CEM I), the addition of ground granulated blast furnace slag (GGBS) in the amount of 0-60 % by mass of the cement, and the addition of siliceous fly ash (FA) in the amount of 0-30 % by mass of the cement. One constant mix composition with W/B=0.45 was established for all concretes. The proportions of binder constituents were subject to changes in particular series, whereas the sum of these constituents, B= (CEM I+GGBS+FA) was constant. The testing programme for both the pastes and the concretes was developed based on the mix design (Fig. 1). Research planning is performed for the system of coordinates of pseudo-components. After the tests, regression coefficients of the equation were calculated in the pseudo-component coordinates: Y = f(A, B, C). The relationship between the binder composition and its properties was investigated not over the entire area of component concentration changes, $0 \le Zi \le 1$, but only within a local section (Table 1).

Table 1. Range of variation in factors investigated.

Real values	Coded values
$0 \le FA \le 30$	$0 \le A \le 1$
C = 1 – (FA + GGBS)	B = 1 – (A + C)
$0 \le GGBS \le 60$	$0 \le C \le 1$

When planning and investigating the composition-characteristic relationship, the characteristic under investigation is assumed to be a continuous function of the investigated variables and can be presented to a satisfactory accuracy as polynomials of typically complex character. Scheffer’s ten-point simplex design for three components was suitable for the third degree polynomial (10 regression coefficients, a_i):

$$Y = a_1*A+a_2*B+a_3*C+a_4*A*B+a_5*A*C+a_6*B*C+a_7*A*B*C+a_8*A*B*(A-B)+a_9*A*C*(A-C)+a_{10}*B*C*(B-C).$$

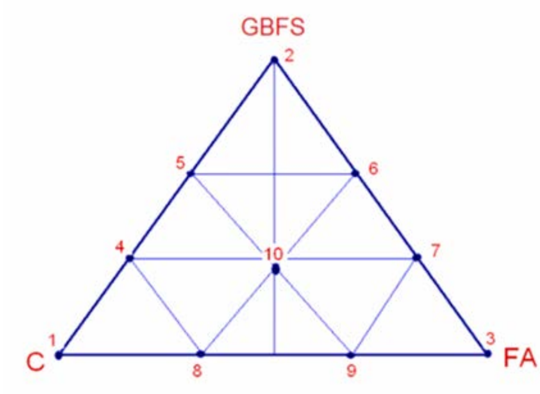

Fig. 1. Mix design with points assigned to pseudo-components.

The test specimens were made with Portland cement, CEM I 42,5N NA, ground granulated blast furnace slag (GGBS) and siliceous fly ash (FA), whose particle size distributions are shown in Fig. 2. The constant water-to-binder ratio for the pastes was taken to be W/B=0.40. Total binder content was constant, as was the amount of mixing water. The contents of the slag and fly ash in the binder were varied.

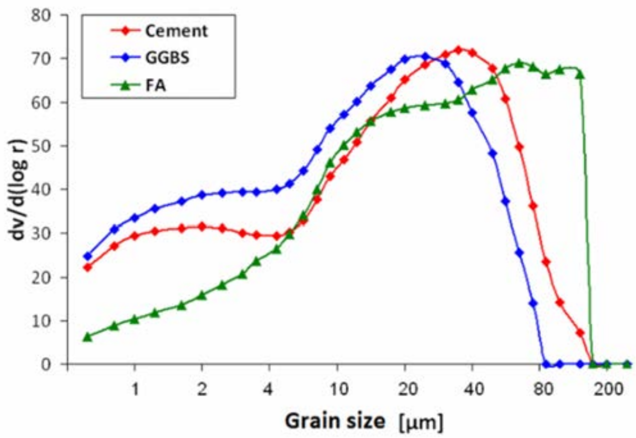

Fig. 2. Grading of cement, slag and fly ash for differential distribution.

The W/B ratio for the concretes was kept constant and amounted to 0.45. As in the case of cement pastes, the cumulative amounts of the binder and mixing water were constant. The contents of the slag and fly ash in the binder were varied. The aggregate composition for the concretes comprised three constituents of constant amounts: natural sand fraction 0/2 mm, basalt aggregate fractions 2/8 and 8/16 mm (32%:34%:34%). S3 slump class concrete was obtained by adding a superplasticizer in the range 0.40÷0.55% by mass of the cement.

After thorough mixing, the samples were put in Ø15/100 mm glass tubes, sealed and left to cure for 90 days. Thereafter, after removing the glass, fragments were taken for analysis. The tests were performed on fracture surfaces; one surface was used for MIP analyses, the other surface was examined by SEM. The measurement of porosity by MIP was conducted using the Micromeritics AutoPore IV Model 9500, which can determine a broad pore size distribution (0.003 to 360 μm). The high-resolution environmental SEM Quanta FEG 250 was used to obtain images of cement paste microstructures. Prior to the observations, the samples were sputtered with gold under high vacuum conditions (EFD). The tests for concrete compressive strength were performed according to PN-EN 12390-3:2011. Absorption was measured in accordance with the Polish standard, PN-88/B-06250. Chloride permeability of concrete was measured by RCPT as stated in ASTM C 1202-12. Surface scaling resistance was determined in the slab test performed in accordance with PKN-CEN/TS 12390-9:2007.

3. Results and Discussions

3.1. Analysis of the cement paste test results

Table 2 summarizes the results from the microporosity tests conducted for the cement paste using the MIP method. The properties tested were porosity (*PORO*), pore area (*POW*), medians (d_m) and average pore diameter (d_{av}).

Table 2. Input factors in coded values and porosity results.

Point	A:FA	B:Cement	C:GGBS	W/C	*POW*, cm^2/g	*PORO*, %	d_{av}, nm	d_m, nm
P1	0	1	0	0.40	26.25	21.74	19.0	34.5
P2	0	0	1	0.63	41.35	24.94	14.5	29.9
P3	1	0	0	0.51	45.47	28.58	15.5	27.6
P4	0.667	0.333	0	0.47	39.74	26.09	15.6	29.0
P5	0.333	0.667	0	0.43	28.77	23.89	19.7	34.8
P6	0	0.667	0.333	0.47	29.00	22.91	18.4	38.8
P7	0	0.333	0.667	0.55	34.31	23.90	16.5	33.8
P8	0.333	0	0.667	0.59	38.04	22.58	13.6	27.8
P9	0.667	0	0.333	0.55	36.09	23.16	14.9	29.7
P10	0.333	0.333	0.333	0.51	34.08	24.93	17.6	35.9

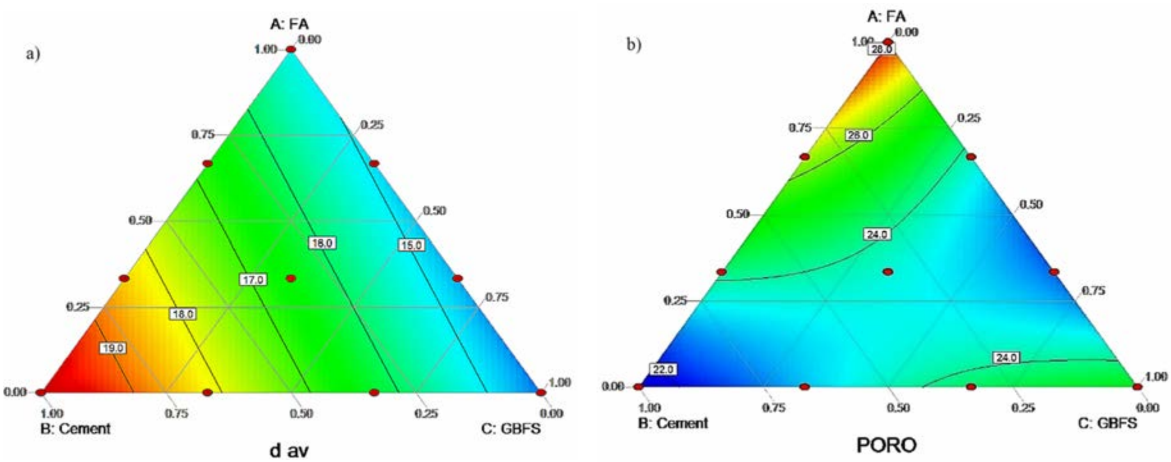

Fig. 3. (a) Average pore diameter (d_{av}); (b) Porosity (*PORO*).

Relationships between the composition of the binder and its properties were developed in the form of a polynomial.

Analysis of contour plots reveals the influence of the mineral additions on the parameters of microporosity of the paste. The dependence of paste porosity (*PORO*) and average pore size (d_{av}) on the type and amount of the addition used is shown in Fig. 3. Taking into account the constant value of W/S=0.40, the change in the binder composition has a negligible effect on the pore size distribution (Fig. 3 a). A slight variation of the predominant pore diameter was observed: 19.0 nm for pure Portland cement, 15.5 nm for the cement with the addition of 30% FA and 14.5 nm for the cement with the addition of 60% GGBS.

The results indicate that the mineral additions increase the pore area and slightly increase the porosity of the paste. The lowest values of porosity (21.74%) and pore area (26.25 cm^2/g) were recorded for the cement paste with Portland cement, CEM I. The highest porosity (28.58%) and the largest pore area (45.47 cm^2/g) were recorded for the paste containing 30% fly ash.

3.2. Tests of concrete

There has been obtained test results after 28 days of curing – absorption n_w, permeability Q, compressive strength f_c, and resistance to surface scaling (slab test) m_{56} - are summarized in Table 3.

Table 3. Test results for concrete.

Point	A:FA	B:Cement	C:GGBS	W/C	n_w, %	Q, Coulomb	f_c, MPa	m_{56}, kg/m^2
C1	0	1	0	0.45	4.23	2631	72.8	1.05
C2	0	0	1	0.72	4.15	1338	60.9	1.43
C3	1	0	0	0.59	4.36	2955	57.7	5.51
C4	0.667	0.333	0	0.54	4.45	2732	58.6	3.13
C5	0.333	0.667	0	0.50	4.39	3169	70.4	2.80
C6	0	0.667	0.333	0.54	4.24	2108	68.9	0.87
C7	0	0.333	0.667	0.63	4.22	1558	65.2	2.77
C8	0.333	0	0.667	0.68	4.33	1562	72.9	3.17
C9	0.667	0	0.333	0.63	4.51	2376	56.5	3.48
C10	0.333	0.333	0.333	0.59	4.35	2563	70.5	2.19

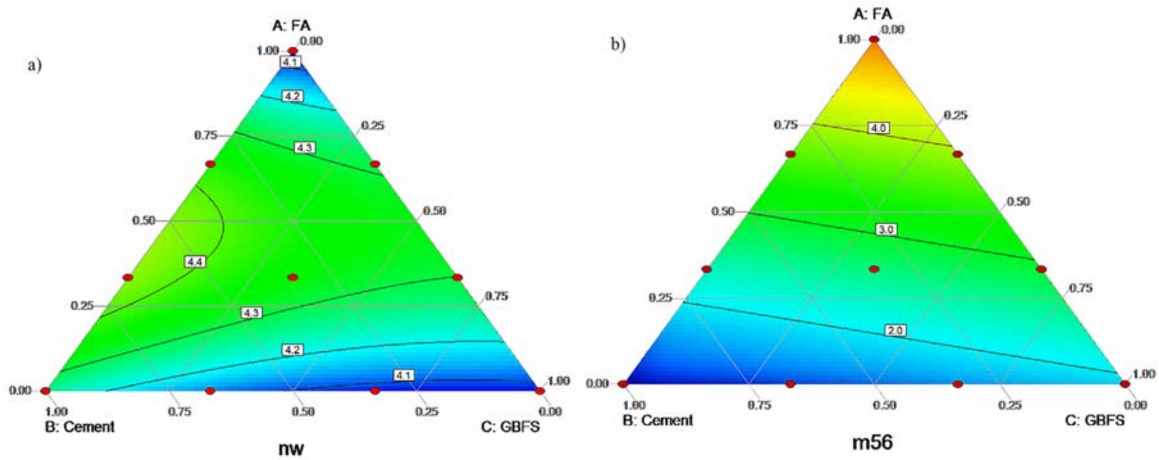

Fig. 4. (a) Absorption; (b) Resistance of concrete to surface scaling.

The dependence of absorption (n_w) on the type and amount of the addition used is shown in Figure 4 a. Figure 4 b shows the contour plot for the resistance to surface scaling. Results from the absorption tests vary within a very narrow range from 4.15% to 4.51%. Analysis of the plots indicates that the value of absorption decreases with increasing amount of the slag. The results of permeability also indicate a reduction when the slag content increases. With 40% slag addition, the value of permeability decreased by nearly 60% relative to CEM I, and with 60% slag content, permeability reduction doubled. When additional portion of fly ash is added, absorption increases slightly. The permeability of concretes containing fly ash is quite high.

The quantity of the material from scaling was considerable and ranged from 0.9 to 5.5 kg/m^2. The least damage was observed in the concrete with the 20% slag addition and the concrete with Portland cement. The highest damage was recorded for concretes with the largest fly ash content.

4. Conclusions

Results of the tests on cement pastes indicate that an increase in the mineral addition amount results in an increase of the pore area and paste porosity. A change in the binder composition by the addition of slag or fly ash causes minor changes in pore size distribution in the cement paste. The predominant pore diameter for pure Portland cement is 19.0 nm. When FA is added at 30%, the pore diameter is 15.5 nm, with 14.5 nm when GGBS is used at 60%.

A change in the binder composition has a minor effect on the results of absorption in concrete, but the value of absorption tends to decrease with increasing slag content. The value of absorption tends to increase with increasing fly ash content. Increased content of slag leads to an evident reduction of permeability of concrete. Permeability is quite high in concretes with fly ash addition.

Freeze-thaw resistance of concrete decreases with increasing content of fly ash. The concrete behaves as expected up to the slag level of 20% by mass of the cement, but above this value the quantity of the material from surface scaling increases. The obtained freeze-thaw test results indicate that the mineral additions do not always provide sufficient impermeability and/or frost resistance to the structure of concrete. From a practical perspective, the application of fly ash or a mixture of fly ash and slag as concrete additions is impractical. The addition of slag is a better solution provided little amount is used. The results from the tests conducted on non-air entrained concretes with W/B ratio of 0.45 (limiting value for concrete exposure class XF4) show that the concrete mix in any case should be air entrained when mineral additions are to be used.

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